Robust *ab initio* calculation of condensed matter: transparent convergence through semicardinal multiresolution analysis

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We present the first wavelet-based all-electron density-functional calculations to include gradient corrections and the first in a solid. Direct comparison shows this approach to be unique in providing systematic "transparent" convergence, convergence with *a priori* prediction of errors, to beyond chemical (millihartree) accuracy. The method is ideal for exploration of materials under novel conditions where there is little experience with how traditional methods perform and for the development and use of chemically accurate density functionals, which demand reliable access to such precision.

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Over the last several decades, the *ab initio* density-functional approach, which replaces the many-body wave function with a set of single-particle "Kohn-Sham" orbitals moving in an effective potential[1], has opened to first-principles study a diverse array of condensed matter phenomena ranging from plasticity, diffusion and surface reconstruction to melting and chemical reactions[2]. While density-functional theory is exact in principle, the true form of the effective potential as a functional of the orbitals is unknown. Current research is pushing available approximations to this functional toward *chemical accuracy*[3], typically defined as predicting bond-breaking energies to 1 kcal/mol = 1.6 millihartree. The prime motivation for this precision is the ability to predict rates of microscopic processes at room temperature, where the relevant energy scale is $k_{\rm B}T \approx 1$ millihartree.

Unfortunately, current feasible representations for the Kohn-Sham orbitals, such as the plane-wave pseudopotential approach[2] or the atomic sphere methods[4], are not easily improved systematically to millihartree accuracy. For instance, although plane-wave bases converge systematically with basis size, pseudopotential calculations require significant experience in the construction of reliable potentials[2]. And, although atomic sphere methods use the Coulomb potential of the nuclei directly, they remain also an art involving many parameters and requiring significant expertise to ensure millihartree accuracy consistently[5]. As testimony to these difficulties, it is not uncommon to find in the literature disagreements over the predictions of density-functional theory.

To illustrate this, Table I presents the lattice constant, cohesive energy and bulk modulus of a very simple solid, MgO in its rock-salt structure, both as measured in experiments[6, 7, 8] *and* and as calculated within the local spin-density approximation (LSDA) when using various representations for the Kohn-Sham orbitals[9, 10, 11, 12, 13]. No two methods in the table agree consistently on the predictions of LSDA. For each property, the spread in predictions is on the order of the discrepancy from the experiment. Without direct estimation of the errors, it is difficult to judge how much of each discrepancy is inherent in LSDA or due to biases built into the different representations. Hence, the use of existing methods is questionable when exploring materials under novel conditions where there is little experience with how such methods perform, as in the study of materials at geological pressures under which atomic cores begin to overlap. (There is recent interest in *ab initio* study of MgO under such conditions[14].) Finally, lack of consistent access to millihartree precision hampers development and eventual use of chemically accurate functionals.

	a [Å]	E_{coh} [eV]	B [Mbar]
Experiment[6, 7, 8]	4.21	10.33	1.55 – 1.62
LMTO[9]	4.09	10.67	1.71
FP-LMTO[10]	4.16		
FP-LAPW[11]	4.167		1.72
pseudopotential[12]	4.191	9.96(+0.5)	1.46
pseudopotential[13]	4.125	11.80	1.56

TABLE I: Structural properties of MgO

The purpose of this letter is to demonstrate for the first time that a new general representation, a wavelet-like multiresolution analysis, provides for solid-state electronic structure calculations an unprecedented level of precision and a new capability for *transparent convergence*, systematic convergence with an extremely simple and predictable scaling for the errors. We also demonstrate the first wavelet calculations to employ generalized gradient approximations (GGAs). We find GGAs to fit seamlessly within our approach, without special concerns such as the discontinuities at the sphere boundaries which arise in the atomic sphere methods[15].

To date, the application of multiresolution analysis to *ab initio* calculations has been limited solely to very simple systems, such as single-electron atoms[16], the diatomic hydrogen molecule[17], diatomic oxygen us-

ing pseudopotentials[18], purely electrostatic problems without electronic structure[19], or all-electron calculations of atoms[20]. Only recently have all-electron wavelet calculations of small molecules appeared in the literature[21, 22]. Here, new techniques[23, 24] enable us to present the first such calculations in solids and the first to include gradient corrected density functionals.

Multiresolution analysis — A multiresolution analysis consists of a basis set of spatially localized functions which describe fluctuations on a hierarchy of length scales, each separated by a factor of two, with the basis functions representing each of these levels of resolution organized on simple rectilinear grids. (Ref. [24] provides a detailed review.) The central, nontrivial mathematical result of multiresolution analysis is that, with appropriately chosen basis functions, this multilevel description is mathematically equivalent to a uniform grid of basis functions on the finest level of resolution[25, 26]. This key result allows for *a priori* knowledge of convergence. In particular, the use of third-order interpolating basis functions in the present work implies that all errors scale as the fourth power of the spacing on the finest level, a factor of sixteen for each additional level of resolution.

The superiority of the multiresolution analysis over the uniform representation comes from the unique way in which the analysis represents information. Because fine-scale coefficients carry information only about high spatial frequencies, they drop rapidly to zero with distance away from the nuclei[21, 24]. Thus, *restriction* of the basis, elimination of functions from finer levels far from the nuclei, has controllably negligible effect on the outcome of the calculation. In practice, sufficient functions can be restricted from the basis so that the basis size and workload grow linearly with the number of levels of resolution, making convergence exponential with basis size[20, 21].

The primary reason for the limitation of wavelet calculations to very simple systems in the past has been the lack of efficient algorithms suited to the solution of non-linear partial differential equations. We recently introduced new algorithms[23, 24] which are faster than the approaches used in the older wavelet electronic-structure works by some three to four orders of magnitude. With these methods, all-electron calculations now require an effort of the same order of magnitude as their pseudopotential counterparts[22], opening the possibility of all-electron wavelet calculations of non-trivial systems.

Given a multiresolution representation, our density-functional calculations proceed by straightforward expansion of the Kohn-Sham Lagrangian[24, 27] or, equivalently, energy functional[1], employing nuclear potentials constructed as described in [22] and employing either the Vosko, Wilk and Nussair parameterization (VWN) of LSDA[28, 29] or the Perdew, Burke and Ernzerhof parameterization (PBE96) of GGA[30]. The calculations then locate the stationary point of the functional using standard preconditioned conjugate gradient methods with analytic continuation as in [31] to maintain the orthonormality constraints among the Kohn-Sham orbitals.

Refs. [22, 24] give the full details of our implementation, with the exception of four extensions which proved critical in carrying out calculations in solids to high precision: (1) treatment of boundary conditions for Bloch states, (2) symmetrization of the electron density, (3) expansion of the electron density on higher resolution grids, and (4) the extension of our approach to include gradient corrections to the exchange-correlation energy.

(1) In a finite multiresolution basis, the common practice of expanding the periodic parts $u_{nk}(r)$, rather than the full Bloch orbitals $\psi_{nk}(r) = e^{ikr}u_{nk}(r)$, does not ensure *extensivity*, that decreasing cell size while correspondingly increasing Brillouin-zone sampling results in identical total energies. However, because wavelet bases share the translational symmetries of the lattice, their expansion coefficients satisfy a discrete Bloch's theorem, $c_{x+R} = e^{ikR}c_x$, where c_x and R are, respectively, the expansion coefficient for the basis function centered at x and any lattice vector. We thus implement Bloch states by storing the coefficients c_x for each orbital ψ_{nk} in a single representative cell and producing all needed coefficients c_{x+R} by multiplying the corresponding coefficient c_x by e^{ikR} ("twisted boundary conditions").

(2) For k-point sampling, we use the scheme of Monkhorst and Pack [32] with symmetry folding of the Brillioun zone. For this folding to be exact, the symmetrized electron density must be expandable in a multiresolution basis respecting the symmetries of the crystal. Accordingly, we symmetrize the density with the operator $s \equiv \mathcal{IPJSIPJ}$, composed from the usual real-space symmetrization operator S, a projector onto basis functions which have all symmetry partners P, and the forward $\mathcal{I}$ and inverse $\mathcal{J}$ wavelet transforms of [24]. Moreover, differentiation of the total energy shows that the self-consistent potential requires a further symmetrization with the operator $s^\dagger$, a different operator from s because $\mathcal{J} \neq \mathcal{I}^\dagger$ for non-orthogonal bases.

(3) In our older approach, which samples real-space quantities only at the centers of basis functions[22], errors in approximate evaluation of the total energy dominate errors from incomplete representation of the orbitals. Accordingly, we now save considerable computational effort by expanding the orbitals in a basis of exactly half the spatial resolution of that representing the other quantities. This proves critical to the present calculations and requires the introduction of new transform operators to be described in depth in a forthcoming publication.

(4) Gradient corrections implement simply and naturally within our framework. Using the notation established in [24], the exchange-correlation energy

$$E_{xc} = \int d^3x\; n(x)\epsilon_{xc}\left(\partial_{x_1}n(x), \partial_{x_2}n(x), \partial_{x_3}n(x), n(x)\right)$$

becomes

$$E_{xc} = (\mathcal{J}n)^\dagger\, \mathcal{O}\mathcal{J}\epsilon_{xc}(\mathcal{D}_1\mathcal{J}n, \mathcal{D}_2\mathcal{J}n, \mathcal{D}_3\mathcal{J}n, n), \qquad (1)$$

where n is a vector of values of the electron density at sampling points at the centers of the basis functions, the

$\mathcal{D}_i$ are matrices of values of the ∂_{x_i} derivative of each basis function at each such sample point, and $\mathcal{O}$ is the matrix of overlaps among basis functions. The exchange-correlation potential then follows directly by differentiating (1) with respect to n, which introduces no new operators other than the Hermitian conjugates of the $\mathcal{D}_i$.

Transparent convergence — To illustrate the feasibility of larger calculations in complex systems, we study an eight atom cubic supercell of MgO. Without pseudizing or treating differently the core states or core regions, our results converge directly to the true LSDA/GGA predictions as a function of only three parameters: number of iterations in the self-consistent solution of the Kohn-Sham equations, the number of k-points in the sampling of the Brillouin zone, and the size of the multiresolution basis. The remaining paragraphs of this section address these three parameters one by one.

Despite the broad range of length scales in the calculation, the convergence of conjugate-gradient minimization is extremely good (0.12 digits/iteration), even when compared to that of plane-wave pseudopotential calculations. As [24, 33] discuss, this results from the use of our specific non-orthogonal basis with a simple diagonal preconditioner. This approach achieves millihartree precision (corresponding to six significant figures) within just forty iterations of starting from randomized atomic wave functions. We typically ran eighty iterations.

Exploring convergence with respect to Brillioun zone sampling (with a multiresolution basis somewhat smaller than that which the calculations below employ) we find that that eight k-points, which reduce to one special point at [0.25 0.25 0.25] in the irreducible wedge, suffice to converge the energy to 0.3 millihartree per chemical unit, better than chemical accuracy.

A key, novel result of this work is the simple form of the convergence to the full all-electron result with increasing basis set and the high precisions which this allows us to reach. Figure 1 shows for both LSDA and GGA the total energy per MgO chemical unit as a function of the fourth power of the spacing on the finest level for the multiresolution grids in Table II when truncated at four, five and six levels of refinement. The results demonstrate that the basis convergence of GGA is almost identical that that of LDA, with no adverse effects from the presence of second derivatives of the density in the exchange-correlation potential. The data clearly exhibit the *a priori* expected quartic convergence, thus demonstrating that the restriction of the basis has negligible effect and that the calculation has entered the asymptotic convergence regime where there are no hidden convergence "shoulders". The quality of the linear fit empowers extrapolation to infinite resolution (stars in the figure insets) with an error of only $\sim$14 *micro*hartree, far below the tolerances described for the most accurate of the standard approaches[11]. We also see that, even without extrapolation, six levels of refinement suffice to give the energy to within 0.5 millihartree per chemical unit. Thus, the present approach gives simple, transparent knowledge of the precision of the calculation at any stage. We believe the simplicity of the convergence of multiresolution analysis to the all-electron result in a practical calculation to be unique in the field of electronic structure.

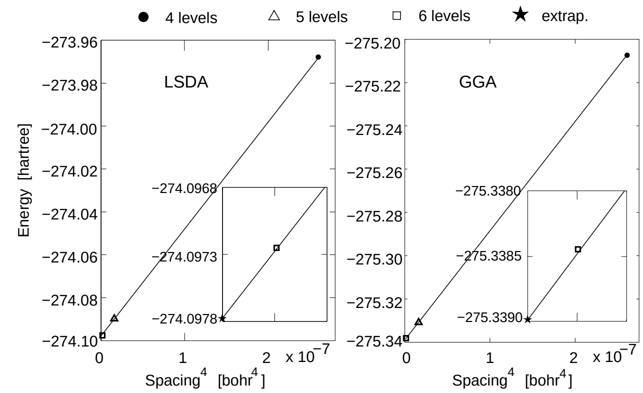

FIG. 1: Convergence of total energy per MgO chemical unit with basis size: LSDA (left panel), GGA (right panel). Insets are comparable in size to square symbols in main plots.

Level	N_x, N_y, N_z	
0	44, 44, 44	
	Mg	O
1	24, 24, 24	24, 24, 24
2	24, 24, 24	24, 24, 24
3	24, 24, 24	28, 28, 28
4	28, 28, 28	28, 28, 28
5	32, 32, 32	32, 32, 32

TABLE II: Restriction employed in the present work: dimension (N_x, N_y, N_z) of the cubic grids of basis functions on the top coarse periodic level (0), and lower levels (1-5) centered on magnesium and oxygen nuclei.

Results — Table III summarizes the predictions of the LSDA-VWN and GGA-PBE96 parameterizations of density-functional theory, when computed with one special k-point and the six-level restriction of the multiresolution analysis from Table II, which the discussion above establishes to give millihartree precision. Note that, to allow direct comparison with the values available in the literature, the table lists the value of the binding energy at the *experimental* lattice constant. Comparison of Table I with Table III shows that, of the traditional methods, only FP-LAPW consistently reproduces the fully converged LSDA results to chemical accuracy. Further, it is now possible to make a definitive determination of the relative transferability among pseudopotentials. Finally, we can now judge unambiguously the predictions of LSDA and GGA for MgO. As generally the case for LSDA, the lattice constant is within a few percent (-1.5%) of the experiment, the system is slightly over bound (+14%), and the bulk modulus is in error by several percent (5-10%, depending upon to which ex-

	a [Å]	E_{coh} [eV]	B [Mbar]
LSDA	4.161±0.003	11.80±0.03	1.71±0.03
GGA	4.221±0.004	11.90±0.03	1.64±0.03
		10.4†	

†Including estimate for spin-polarization energy of atomic oxygen based on LSDA/LDA difference of 1.5 eV.

TABLE III: Multiresolution analysis calculation of structural properties of MgO within LSDA and GGA.

periment we compare). For GGA relative to LSDA, we find the typical expansion of the lattice constant, correction of the over-binding (when including atomic spin-polarization energies) and decrease in the bulk modulus. For MgO, GGA improves these results dramatically.

Conclusions — We report the first solid-state all-electron calculations within a wavelet-like multiresolution analysis and the first multiresolution calculations to include gradient corrections. The results give the first *independent* verification that, of the traditional methods, FP-LAPW is by far the most accurate and gives the first unambiguous demonstration that GGA outperforms LSDA for MgO. We also demonstrate multiresolution analysis to be unique among electronic-structure representations in exhibiting extremely simple and predictable convergence to far beyond millihartree accuracy. This approach, therefore, is ideal for novel problems such as the study of the impact of core polarization effects on electron energy loss and X-ray absorption spectra and the investigation of materials under geological pressures, applications where the use of the traditional, less systematic approaches remains more an art than a science.

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